Anode activating agent recovery by magnetic separation from the <0.075 mm fraction of crushed nickel metal hydride batteries from hybrid vehicles

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A B S T R A C T

Nickel metal hydride batteries of hybrid vehicles contain rare metals such as Ni, Co, and rare-earth elements as electrode components. A direct smelting method has been used to recover Ni from waste batteries, but the Co and rare-earth elements are difficult to extract with this conventional method. To recycle Co and rare-earth elements, physical pretreatment is necessary to separate the anode and cathode compounds before smelting. This study investigated the magnetic separation of anode and cathode activating agents in the <0.075 mm fraction of crushed cylindrical and prismatic types batteries. In the cylindrical type anode activating agent concentrated in the non-magnetic product of the Davis tube tester, separated at low magnetic fields (0.1 T), while in the prismatic type anode activating agent concentrated in the magnetic product of high gradient magnetic separation. Microscope observations and results of the elemental analysis with energy dispersive X-ray spectroscopy showed that this separation behavior difference originates from differences in the cathode component manufacturing processes. An optimum physical treatment process using magnetic separation is proposed to recover the rare metal components.

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1. Introduction

Nickel metal hydride (Ni-MH) batteries are used in hybrid vehicles and such batteries contain Ni-hydroxide and Co-hydroxide as the cathode activating agent and an alloy of Ni and misch metal (mM), a rare-earth element mixture consisting of La, Ce, Nd, and Pr as the anode hydrogen adsorption component. In conventional recycling, Ni and Fe (used in the case and substrate components) are recovered with a rotary kiln-electric melting process and the Co and mM go to the slag component [1]. To recover both the mM and other valuable components Zhang et al. [2,3] and Tzanetakis and Scott [4,5] proposed a chemical process using acid dissolution and solvent extraction and Pietrelli et al. [1] proposed a process where the mM and Ni were recovered as sulfates with a selective precipitation method after dissolution in sulfuric acid. In these methods both the anode (alloy of Ni and mM) and cathode (Ni-hydroxide) activating agents are dissolved in acid solutions but if the anode activating agent can be separated from the cathode activating agent before the dissolution it would become possible to

recover, the anode activating agent as the original alloys without acid dissolution and reduction treatments. Wang et al. [6] reported that high purity Ni–mM alloy can be recovered from waste anode activating agent using a melting method. This report describes the magnetic separation of anode and cathode activating agents in the <0.075 mm fraction of crushed batteries, and proposes a practical treatment process for cylindrical and prismatic types batteries.

2. Materials and outline of physical and chemical treatment combining process

The authors and Japan Oil, Gas and Metals National Corporation have proposed a physical and chemical combining treatment process of Ni-MH batteries [7]. The first stage is a physical separation process to recover each component from crushed product and the second stage is a chemical treatment process wherein the cathode and anode activating agents (recovered in the first stage) are treated by acid dissolution and alloy melting, respectively. The <0.075 mm fraction of the crushed batteries contains anode activating agent as a major component and cathode activating agent as a minor component but further separation is needed for the subsequent chemical treatment stage. The acceptable purity of anode activating agent in the physical separation concentrate is estimated to be about 90% leaving only a small amount of impurity for the chemical treatment stage [8].

Batteries were crushed with a double-shaft type crusher after being cooled in liquid N_2 for deactivation. The crushed products

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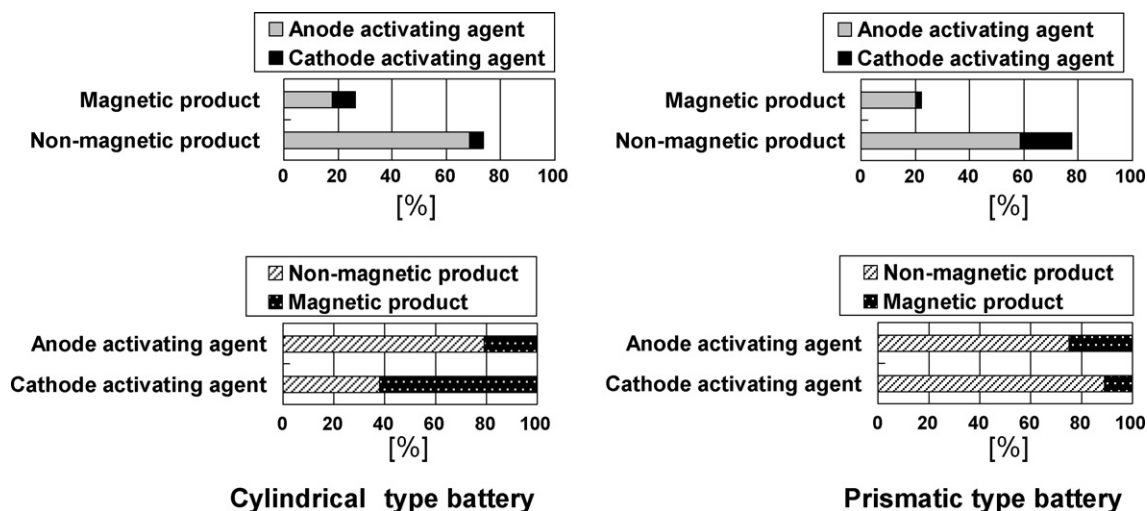
Fig. 1. Results of magnetic separation using the Davis tube tester. The magnetic product shows the total of the 1st, 2nd, and 3rd stage treatments.

are less than about 40 mm in size and can be divided into a coarse fraction and a fine fraction smaller than 1 mm. The authors have developed a distance variable magnetic separation method to separate the anode and cathode substrates contained in the >1 mm fraction [7]. The <1 mm size fraction contains the anode and cathode activating agents detached from the substrate in the crushing process. This <1 mm fraction was classified into two (<0.075 and >0.075 mm) by sieving and then analyzed. The 1–0.075 mm size fraction contained the cathode activating agent as a major component and the anode activating agent as a minor component. The purity of the cathode activating agent in this fraction is high and this fraction can be treated chemically. The <0.075 mm size fraction obtained from the cylindrical and prismatic type batteries contains both anode and cathode activating agents and was used in the following experiments.

The authors has developed a size distribution measurement method of the mixture of anode and cathode activating agent (fine fraction of crushed product) using back scattered electron images and image analysis software [9] and the measured mean particle diameter of the anode and cathode activating agents in the <0.075 mm fractions is 0.052 mm (cylindrical), and 0.021 mm (prismatic) for the cathode component; and 0.014 mm (cylindrical), and 0.033 mm (prismatic) for the anode component. The specific gravity was measured by the Ultra Pycnometer 1000, Yuasa Ionics Inc. and the values were 4.7 (cylindrical) and 4.5 (prismatic) for the cathode component and 7.2 (cylindrical) and 6.8 (prismatic) for the anode component.

3. Magnetic separation of the <0.075 mm fraction

Wet magnetic separation using the Davis tube tester, model EDT, Eriez Magnetics Japan Co. Ltd., was carried out in three stages at low magnetic fields. The non-magnetic product of the 1st stage (0.1 T, the magnetic field strength at the center of the tube) was supplied to the 2nd stage (0.2 T) and the non-magnetic product of the 2nd stage was supplied to the 3rd stage (0.3 T) to avoid entrapment. The sample was added to pure water and this slurry was fed from the top of the tube. Experiment was carried out at solid concentration of 10%, angle of rotation of 120°, stroke of 50 mm, and for 3 min.

La and Ce are contained only in the anode activating agent and basically, the content ratios of the anode and cathode activating agent were calculated from the analytical data of La and Ce by X-ray fluorescence analysis (JSX-3201A, JEOL Co., Ltd.). However the difference between the calculated values of content ratios of the anode and cathode activating agent was less than 1%. Since La concentration was larger than that of Ce, only La was used in the calculation of content ratios of the anode and cathode activating agent of the samples. The standard error in the calculated ratios of anode and cathode activating agent in eight feed samples using analytical data of La was ±0.9%.

Fig. 1 and Table 1 show the results of the three stage magnetic separation. The separation results were different for the cylindrical and prismatic types and good results were obtained for the cylindrical type; anode activating agent was concentrated in the non-magnetic product with a final purity of 93% where

Table 1
Results of three stage magnetic separation using the Davis tube tester.

	Recovery of anode activating agent (%), as non-magnetic product	Purity of anode activating agent (%), as non-magnetic product	Over-all separation efficiency (%)
(a) Cylindrical type			
Feed		86	
Stage 1 (0.1 T)	97	88	8
Stage 2 (0.2 T)	89	91	27
Stage 3 (0.3 T)	79	93	41
	Recovery of anode activating agent (%), as magnetic product	Purity of anode activating agent (%), as magnetic product	Over-all separation efficiency (%)
(b) Prismatic type			
Feed		79	
Stage 1 (0.1 T)	1	82	0.1
Stage 2 (0.2 T)	7	85	3
Stage 3 (0.3 T)	26	90	15

Table 2
Results of high gradient magnetic separation of prismatic type sample. The magnetic field strength is a value at the center of the empty separation chamber.

	Recovery of anode activating agent (%), as magnetic product	Purity of anode activating agent (%), as magnetic product	Over-all separation efficiency (%)
Feed		80	
0.1 T	63	92	41
0.2 T	93	89	47
0.3 T	95	89	45
0.4 T	97	87	39

the feed purity was 86%. Final recovery of anode activating agent was 79% and over-all separation efficiency was 41%. The over-all separation efficiencies (Newton efficiency) are calculated by Eq. (1) [10].

Over-all separation efficiency

= 'recovery ratio of material for concentration'

+ 'removal ratio of unwanted material' − 100   (1)

With the prismatic type the Davis tube tester could not remove cathode activating agent as magnetic product and anode activating agent was slightly concentrated in the magnetic product. Thus wet high gradient magnetic separation using HIW L-4, Eriez Magnetics Japan Co., Ltd., was carried out for the prismatic type sample. Treatment was carried out in four different applied magnetic fields: 0.1, 0.2, 0.3, and 0.4 T (the value is the magnetic field strength at the center of the empty separation chamber). The sample was added to pure water and the slurry was fed from the top at 400 cm^3/min. Batch experiment was carried out at solid concentration of 20% using matrix materials (SUS410, lattice-shaped matrix of 1 cm aperture size, and wire diameter of 1.5 mm). Table 2 shows the results of the high gradient magnetic separation of the prismatic type sample. Anode activating agent was concentrated in the magnetic product with the purity of 89% when the applied magnetic field is 0.2 and 0.3 T where the feed purity was 80%. The recovery of anode activating agent was 93% (0.2 T) and 95% (0.3 T) and the over-all separation efficiency was 47% (0.2 T) and 45% (0.3 T). These results show that the magnetic separation method is useful but that separation behavior is different for the cylindrical and prismatic type samples.

4. Discussion and proposal of treatment process of cylindrical and prismatic batteries

Anode activating agent is an alloy of Ni and mM and the measured values (mass criterion, m^3/kg) were 94 for the prismatic type and 315 for the cylindrical type. Cathode activating agent is chiefly composed of Ni-hydroxide and the relative magnetic susceptibility of Ni-hydroxide reagent (measured value, mass criterion, m^3/kg) is 29. The relative magnetic susceptibility of anode activating agent is higher than that of Ni-hydroxide. Therefore anode activating agent of the prismatic type was concentrated as magnetic product by the high gradient magnetic separator.

In the Davis tube tests 21 and 25% of anode activating agent was recovered as magnetic product for the cylindrical and prismatic types, respectively (Fig. 1). On the other hand 62% of the cathode component was recovered as magnetic product in the cylindrical type and 11% for the prismatic type as shown in Fig. 1 indicating that the attraction force of the cathode activating agent in the cylindrical type is stronger than that of the anode activating agent. Fig. 2 shows a microscope image of the cathode component of cylindrical type sample and the energy dispersive spectroscopy (EDS) results by point analysis show that the bright color part is Ni metal

and the dark part is Ni-hydroxide. The bright Ni parts are very small and narrow (width less than 1 μm) and this indicates that the cathode particles may be a middling product of Ni-hydroxide and Ni metal. The relative magnetic susceptibility of Ni metal is very high, 5140 (measured value, mass criterion, m^3/kg), and it is expected that the cathode component of the cylindrical type was recovered as magnetic product at low magnetic fields by the Davis tube tester. This may be attributed to different manufacturing processes of cathode components. In the manufacturing process of the cylindrical type cathode, the cathode activating agent (Ni-hydroxide) is deposited on a plaque of Ni metal substrate (porous with pore size 6–12 μm) by chemical or electrolytic deposition. With the prismatic type cathodes, activating agent (a paste of Ni-hydroxide and cellulose thickener) is filled into an already formed Ni substrate (pore size bigger than the cylindrical cathode) and dried at a relatively low temperature. The EDS results may show that the cathode component of the cylindrical type contains Ni plaque, a part of the substrate, and that Ni plaque is detached from substrate together with activating agent during the crushing treatment.

The purity of the recovered anode activating agent of both the cylindrical and prismatic types is high, about 90%, and this product can be treated effectively in the chemical treatment stage. Fig. 3 shows proposed integrated treatment flow charts. The less than 0.075 mm fraction is treated by wet magnetic separation in high gradient (prismatic) or low magnetic fields (cylindrical) and anode activating agent of high purity is obtained. The over 1 mm fraction is treated with dry magnetic separation and low impact breaker and separated as iron component (nuts and bolts, anode substrate, cylindrical type cathode substrate, cylindrical type case), Ni metal (prismatic type cathode substrate), plastics (separator and prismatic type case), anode activating agent, and cathode activating agent [7]. The iron component, Ni metal, and plastics are recycled
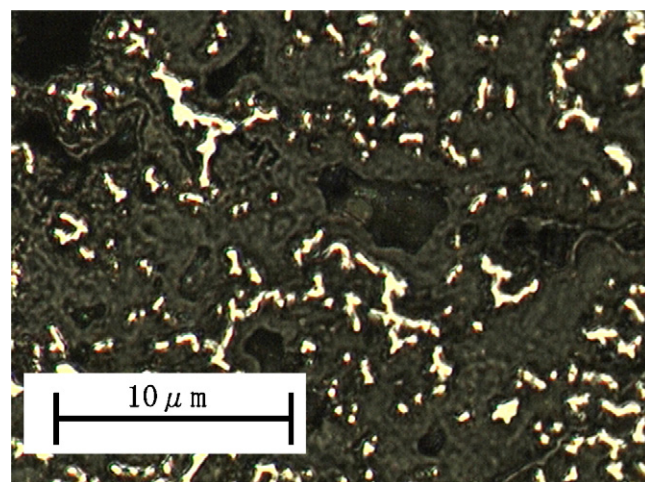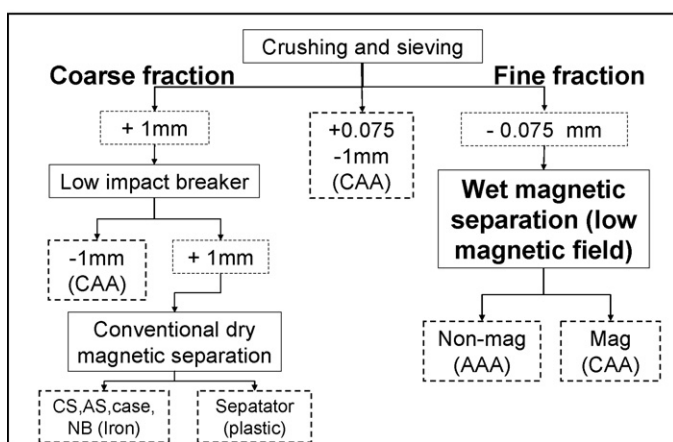

Fig. 2. A scanning electron microscope image of the crushed cathode component of the cylindrical type battery.
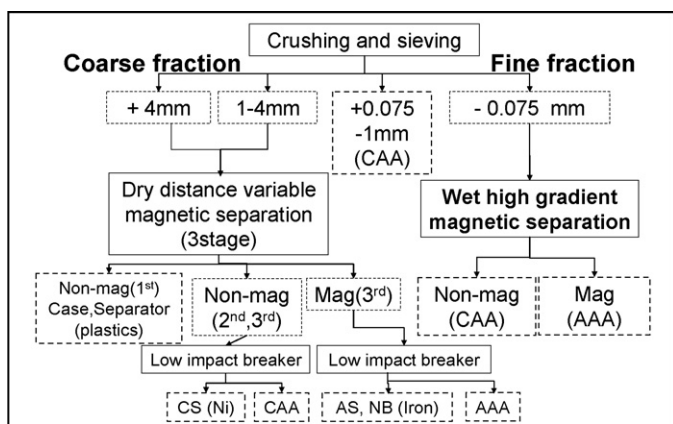
CS: cathode substrate, CAA: cathode activating agent, AS: anode substrate, NB: nuts and bolt, AAA: anode activating agent

(a) **Prismatic type battery**

CS: cathode substrate, CAA: cathode activating agent, AS: anode substrate, NB: nuts and bolt, AAA: anode activating agent

(b) **Cylindrical type battery**

Fig. 3. Treatment flow chart for recovery of valuable components of Ni-MH batteries.

and the cathode and anode activating agents are treated with the appropriate processes separately in the subsequent chemical treatment stage.

5. Summary

Magnetic separation of the fine fraction (less than 0.075 mm) of crushed product of Ni-MH batteries was carried out. Anode activating agent was concentrated in the non-magnetic product with the Davis tube tester for the cylindrical type while for the prismatic type the anode activating agent was concentrated in the magnetic product of the high gradient magnetic separation. This difference originates from the manufacturing process of the cathode component suggesting that appropriate treatment in the recycling process is important.

Acknowledgments

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